

JAPANESE

[JP,2001-089129,A]

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CLAIMS DETAILED DESCRIPTION TECHNICAL FIELD PRIOR ART EFFECT OF THE  
INVENTION MEANS EXAMPLE

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[Translation done.]

(72)

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DETAILED DESCRIPTION

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## [Detailed Description of the Invention]

[0001]

[Industrial Application]This invention relates to the method of manufacturing monolith-like compound silica aerogel outstanding as a precursor of highly efficient thermal insulation, highly efficient catalyst, and highly efficient light material.

[0002]

[Description of the Prior Art]As a method of preparing silica aerogel, conventionally, The moist gel object which contains a solvent in an inside using alkoxysilane is prepared, and there is the method (U. refer to S.P. 4,327,065 specification) of drying by a supercritical state, There is a method (JP,6-227809,A) with which the alcohol solution of metallic compounds is impregnated and which carries out supercritical drying of the silica alcogel after that as a method of manufacturing compound silica aerogel.

[0003]

[Problem(s) to be Solved by the Invention]The silica aerogel obtained by the method of given [ above-mentioned ] in the U.S.P. No. 4,327,065 specification is the low density which the silica particle of the nano meter level condensed to arborescence, and is a very big porous body of voidage and specific surface area.

It is used as a precursor of thermal insulation with low thermal conductivity, or special glass. By composite-izing other metallic components, these can expect the adiathermic improvement by grant of infrared reflective power, the use as a highly efficient catalyst, grant of new optical physical properties, etc.

[0004]However, there was a problem that the structure control of a nano meter level became difficult as the quantity of the composite-ized ingredient increased, since it was influenced by the ingredient which the reaction of alkoxysilane composite-izes when mixing other metallic compounds at the time of preparation of silica moist gel and trying to perform composite-ization. In the method with which silica moist gel is impregnated by the liquid phase in metallic compounds, the case where osmosis in the inside of gel did not take a long time, or it did not permeate enough to an inside with the kind or concentration of a compound of a thing good about control of structure was seen plentifully. Since a presentation was limited as a result or it was accompanied by a crack and modification with the heterogeneity of gel at the time of desiccation and heat treatment, there was a case where compound monolith-like aerogel was not obtained.

[0005]

[The problem which is going to solve an invention] Then, this invention makes it a technical problem to control the structure of a nanometer level enough and to obtain promptly homogeneous high monolith-like metallic-oxide compound silica aerogel.

[0006]

[Means for Solving the Problem]In a method of obtaining silica aerogel which a silica moist gel object is impregnated with this invention, it made it drying a drying medium which mixed metallic compounds, and metallic compounds and a silica particle composite-ized in order to solve an aforementioned problem, By performing both an impregnation process and a drying process by a

supercritical condition of a drying medium, it finds out that monolith-like metallic-oxide compound silica aerogel is obtained efficiently, and came to complete this invention.

[0007]A silica moist gel object in this invention uses a part for silicic acid as the main ingredients, and if it is a substance of jelly state which contains a solvent in an inside, a kind and a preparing method in particular will not be limited. If an example is given, a silica moist gel object acquired by hydrolyzing under existence of an acid catalyst of a base catalyst of ammonia etc. or chloride, for example using a tetramethoxy silane, a silica moist gel object acquired by adding acid, such as chloride, to a sodium silicate solution (water glass), etc. will be used.

[0008]Such silica moist gels impregnate with and respond into a solvent with a medium or it which is beforehand used for supercritical drying, and compatibility, and replace an internal solvent. Although what is necessary is just to choose suitably a medium used for a supercritical drying method according to a kind of composite-sized ingredient, and character and it is not limited in particular, alcohols, carbon dioxide, and these two-component systems, such as methanol and ethanol, are usually used.

[0009]Subsequently, such silica moist gels are sealed by pressure vessel with a drying medium and metallic compounds. Metallic compounds dissolve in a drying medium, and if it is silica moist gel and a substance reacted, or adsorbed and supported, a kind in particular will not be limited. If an example is given, metal acetylacetonate, such as a complex, titanyl acetylacetonate, etc. which embellished metal alkoxides, such as titanium tetraisopropoxide and aluminum NIUMUTORI n-butoxide, and them with a suitable ligand, a derivative of those, etc. will be used.

[0010]temperature-up pressure up of the pressure vessel which sealed silica moist gel was carried out as it was, or it introduced and carried out pressure up of the drying medium using high pressure pumping etc. from the exterior -- after temperature up is carried out and it is held on condition of more than a critical point for 3 to 12 hours. Conditions of a supercritical point are 80 \*\* and 160 atmospheres or more, when it changes with kinds of a drying medium and metallic compounds, for example, the two-component system of alcohol and carbon dioxide is used for a drying medium and it uses titanium tetraisopropoxide acetylacetonate as metallic compounds. Metallic compounds are quickly diffused in silica moist gel under a supercritical condition, and it sticks to a hydroxyl group, a reaction, or a gel surface in gel, and they are supported. then, having held temperature and a pressure -- composite -- it decompresses and dries and aerogel is obtained, after circulating a drying medium which does not contain a transformed part in a pressure vessel for 2 to 3 hours and removing superfluous metallic compounds from inside of a container. ~~Metallic-oxide compound silica aerogel is obtained by heat-treating obtained aerogel above 500 \*\* among the air.~~

[0011]

[Embodiment of the invention] The embodiment of the invention is as follows.

(1) In a method of obtaining silica aerogel which a silica moist gel object is impregnated with, made it drying a drying medium which mixed metallic compounds, and metallic compounds and a silica particle composite-sized, A manufacturing method of monolith-like metallic-compounds compound silica aerogel performing both an impregnation process and a drying process by a supercritical condition of a drying medium.

(2) A complex in which metallic compounds embellished metal alkoxides, such as titanium tetraisopropoxide and aluminum NIUMUTORI n-butoxide, and them with a suitable ligand, A manufacturing method of monolith-like metallic-compounds compound silica aerogel of one above-mentioned statement which is some one of metal acetylacetonate, such as titanyl acetylacetonate, and the derivative of those.

(3) A manufacturing method of monolith-like metallic-compounds compound silica aerogel with which a drying medium was indicated to the above 1 or the above 2 which is alcohols and/or carbon dioxide.

(4) A manufacturing method of monolith-like metallic-compounds compound silica aerogel with which silica moist gel was indicated to any one of the above 1 which is alcogel thru/or the above 3.

[0012]

[Example]Although the example which materialized this invention is shown below, this invention

should not be limited at all by this.

<Example 1> tetramethoxy silane, methanol, and a 0.0135 mol/l aqueous ammonia solution were mixed under 20 \*\* conditions, it slushed and settled into a container 30 mm in inside diameter, and 10 mm in depth, and the moist gel object of silica was acquired. This gel was sealed and it riped at 60 \*\* for 48 hours. Then, removal of unreacted components and solvent exchange were performed by being impregnated exchanging 2-propanol several times on the way in an excessive amount of 2-propanol for 24 hours.

[0013]Next, 25 ml of 2-propanol solutions of titanium tetraisopropoxide acetylacetonate of three pieces and concentration 1.24 mol/l are put for the above-mentioned silica moist gel object in a 50-ml pressure vessel, After-sealing carbon dioxide was introduced, pressure up was carried out to 200 atmospheres, and it heated to 80 more \*\*, and was considered as the supercritical state. The pressure in a pressure vessel was set constant with the pressure regulator. this state -- respectively -- 3 -- it held for 6 or 12 hours, and the above-mentioned titanium compound was combined with the silica moist gel surface.

[0014]Next, supercritical carbon dioxide was circulated at 2 ml/m in the at-the-same-pressure power container for 3 hours, 2-propanol and the above-mentioned titanium compound which remain were removed from the inside of a container, and it changed into the state of only supercritical carbon dioxide. Subsequently, with temperature maintained, carbon dioxide was extracted gradually and it was considered as ordinary pressure so that it might become decompression of 1 atmosphere per minute, and aerogel was obtained. This aerogel was calcinated at 500 \*\* among oxygen, and titania compound silica aerogel was obtained.

[0015]the silica moist gel prepared like the <comparative example 1> example 1 -- 25 ml of 2-propanol solutions of titanium tetraisopropoxide acetylacetonate with a concentration of 1.24 mol/l. -- ordinary temperature ordinary pressure -- respectively -- 3 -- it was impregnated for 6 or 12 hours, and the titanium compound was supported. Next, three pieces and 25 ml of 2-propanol solutions were put for the above-mentioned silica moist gel object in a 50-ml pressure vessel, carbon dioxide was introduced, the pressure was 200 atmospheres, and it heated to 80 more \*\*, and was considered as the supercritical state, and titania compound silica aerogel was obtained like Example 1 henceforth.

[0016]The atomic ratio (the sum total of the atomic number of silicon and titanium is made into 100%) of the titanium contained in the center section (15 mm in diameter and about 5 mm in height) and the other exterior of titania compound silica aerogel produced by carrying out like Example 1 and the comparative example 1 was measured with X-ray fluorescence analysis, and it collected into Table 1.

[0017]

[Table 1]

チタン 含量 含浸時間	実施例 1 中心部分 (%)	実施例 1 外側部分 (%)	比較例 1 中心部分 (%)	比較例 1 外側部分 (%)
3 時間	28.5	42.9	18.6	40.8
6 時間	36.4	43.8	28.5	44.9
12 時間	43.8	47.0	36.4	50.5

[0018]As the above-mentioned table shows, compared with the aerogel of the comparative example 1 in which it was impregnated with the titania compound silica aerogel prepared using being supercritical impregnated of Example 1 in the solution, it turns out that the titanium ingredient has permeated the inside of gel for a short time.

[0019]In example 2 Example 1, concentration of the 2-propanol solution of titanium tetraisopropoxide acetylacetonate is made into 0.618, 0.309, and 0.155 mol/l, respectively, Retention time was made into 12 hours, and also titania impregnating silica aerogel was prepared like Example 1.

[0020]In the comparative example 2 comparative example 1, concentration of the 2-propanol solution of titanium tetraisopropoxide acetylacetonate is made into 0.618, 0.309, and 0.155 mol/l, respectively, Retention time was made into 12 hours, and also titania impregnating silica aerogel

was prepared like the comparative example 1.

[0021]The atomic ratio (the sum total of the atomic number of silicon and titanium is made into 100%) of the titanium contained in the center section (15 mm in diameter and about 5 mm in height) and the other exterior of titania compound silica aerogel produced by carrying out like Example 2 and the comparative example 2 was measured with X-ray fluorescence analysis, and it collected into Table 2.

[0022]

[Table 2]

チタン 含量 濃度 (mol/l)	実施例 1 中心部分 (%)	実施例 1 外側部分 (%)	比較例 1 中心部分 (%)	比較例 1 外側部分 (%)
0.618	33.6	51.4	30.9	39.0
0.309	26.8	39.4	13.9	34.4
0.155	19.1	37.3	8.2	22.8

[0023]As shown in the above-mentioned table, when the concentration of a titanium compound is low, in being impregnated with the solution of the comparative example 2. Although the titanium ingredient has not permeated enough to an inside, in the titania compound silica aerogel prepared using being supercritical impregnated of Example 2. In a supercritical state that the titanium content of the gel central part is improving turns out to be, the viscosity of a solvent will become 1/10 or less [ of a fluid ], and the diffusion coefficient of a substance will generally be 10 or more times. For this reason, diffusion into the fine pores of the silica moist gel of the composite-ized ingredient is promoted, and it is thought that quick and homogeneous composite-ization has been attained.

[0024]

[Effect of the Invention]According to this invention, since it can be impregnated in the more homogeneous state more nearly promptly than the case where you make it impregnated by the liquid phase of ordinary temperature ordinary pressure, the monolith-like compound silica aerogel which supported the metallic oxide can be obtained efficiently.

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CLAIMS

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[Claim(s)]

[Claim 1]In a method of obtaining silica aerogel which a silica moist gel object is impregnated with, made it drying a drying medium which mixed metallic compounds, and metallic compounds and a silica particle composite-ized, A manufacturing method of monolith-like metallic-compounds compound silica aerogel performing both an impregnation process and a drying process by a supercritical condition of a drying medium.

[Claim 2]A complex in which metallic compounds embellished metal alkoxides, such as titanium tetraisopropoxide and aluminum NIUMUTORI n-butoxide, and them with a suitable ligand, A manufacturing method of the monolith-like metallic-compounds compound silica aerogel according to claim 1 which is some one of metal acetylacetonate, such as titanyl acetylacetonate, and the derivative of those.

[Claim 3]A manufacturing method of monolith-like metallic-compounds compound silica aerogel with which a drying medium was indicated to claim 1 or claim 2 which is alcohols and/or carbon dioxide.

[Claim 4]A manufacturing method of monolith-like metallic-compounds compound silica aerogel with which silica moist gel was indicated to any one of claim 1 which is alcogel thru/or the claims 3.